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1,118,742



PATENT SPECIFICATION

NO DRAWINGS

1,118,742

Date of Application and filing Complete Specification: 25 May, 1965.

No. 7051/68.

Application made in United States of America (No. 372,113) on 2 June, 1964.

Application made in United States of America (No. 451,033) on 26 April, 1965.

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Int. Cl.:—D 06 m 13/14

COMPLETE SPECIFICATION

Novel Aqueous Formaldehyde Composition

ERRATUM

SPECIFICATION No. 1,118,742

Page 7, Example IX, Column 3, under *Gauge*
(Dry) for "20" read "30"

THE PATENT OFFICE
10th September 1968

claimed in our copending application No. 22025/65 (Serial No. 1118741).

The alkyl carbamate has the formula:



where R is an alkyl or cycloalkyl group. Thus, there can be employed for example methyl carbamate, ethyl carbamate, propyl carbamate, isopropyl carbamate, butyl carbamate, amyl carbamate, hexyl carbamate, octyl carbamate, decyl carbamate, dodecyl carbamate, cyclohexyl carbamate or octadecyl carbamate. Mixtures of carbamates can be employed, e.g. the eutectic mixture of 52% by weight of ethyl carbamate and 48% by weight of methyl carbamate.

Throughout the present specification, unless otherwise indicated, all parts and percentages are by weight.

Preferably, the alkyl carbamate employed is a lower alkyl carbamate; most preferably

materially reduced.

The mixture of formaldehyde and alkyl carbamate, e.g. formaldehyde and methyl carbamate, can be shipped as an aqueous mixture containing the two materials in any of the proportion indicated above. This aqueous mixture can be relatively concentrated at the time of shipment and can then be diluted with water to obtain the desired amount of ingredients for the bath through which is passed the cotton, for example. For stability purposes, the mixture which is shipped is preferably neutral, although it can be alkaline or acidic.

Of course, there can be added to the aqueous mixture of aldehyde and alkyl carbamate conventional additives, such as wetting agents, hand modifiers, softeners, lubricants and brighteners.

The following Examples illustrate the novel aqueous compositions of the invention and their use in the treatment of cellulosic textile materials according to the process of copend-

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Int. Cl.:—D 06 m 13/14

COMPLETE SPECIFICATION

Novel Aqueous Formaldehyde Composition

We, WEST POINT-PEPPERELL INC., a Corporation of the State of Georgia, United States of America, of West Point (No Street Address), Georgia, United States of America, (Assignee of JAMES FRANK COTTON and MAURICE EARL HEARD), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel aqueous formaldehyde composition.

According to the present invention a composition of matter is provided comprising an aqueous mixture of formaldehyde and an alkyl carbamate wherein the mole ratio of formaldehyde to carbamate is at least 3:1.

The aqueous mixture may be used for fixing formaldehyde on cellulose, a cellulose ester or starch according to the process described and claimed in our copending application No. 22025/65 (Serial No. 1118741).

The alkyl carbamate has the formula:



where R is an alkyl or cycloalkyl group. Thus, there can be employed for example methyl carbamate, ethyl carbamate, propyl carbamate, isopropyl carbamate, butyl carbamate, amyl carbamate, hexyl carbamate, octyl carbamate, decyl carbamate, dodecyl carbamate, cyclohexyl carbamate or octadecyl carbamate. Mixtures of carbamates can be employed, e.g. the eutectic mixture of 52% by weight of ethyl carbamate and 48% by weight of methyl carbamate.

Throughout the present specification, unless otherwise indicated, all parts and percentages are by weight.

Preferably, the alkyl carbamate employed is a lower alkyl carbamate; most preferably

methyl carbamate, ethyl carbamate or a mixture thereof.

The formaldehyde is employed in the aqueous system in an amount normally between 1% and 8% thereof, although if relatively larger amounts of formaldehyde are to be fixed on to the cellulose or other material, there can be used as much as 10% or 15% or more of formaldehyde. The formaldehyde is desirably present in an amount of 3.5 moles per mole of carbamate and can be employed in an amount as much as 60 moles or even 100 moles per mole of carbamate. Generally, lower mole proportions of formaldehyde are preferred, and one of the advantages of the present invention is that lower amounts of formaldehyde are required in the aqueous treating system, for the amount of formaldehyde fixed on the cellulosic material, than is the case with prior art processes. Additionally, the problem of formaldehyde odour is thereby materially reduced.

The mixture of formaldehyde and alkyl carbamate, e.g. formaldehyde and methyl carbamate, can be shipped as an aqueous mixture containing the two materials in any of the proportion indicated above. This aqueous mixture can be relatively concentrated at the time of shipment and can then be diluted with water to obtain the desired amount of ingredients for the bath through which is passed the cotton, for example. For stability purposes, the mixture which is shipped is preferably neutral, although it can be alkaline or acidic.

Of course, there can be added to the aqueous mixture of aldehyde and alkyl carbamate conventional additives, such as wetting agents, hand modifiers, softeners, lubricants and brighteners.

The following Examples illustrate the novel aqueous compositions of the invention and their use in the treatment of cellulosic textile materials according to the process of copend-

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ing application No. 22025/65 (Serial No. 1118741).

EXAMPLE I

Generally, the border yarns in towels shrink more than the rest of the towel. In order to overcome this defect, a series of towel border cotton yarns were treated in a kier with an aqueous mixture containing 1% methyl carbamate, 0.5% magnesium chloride hexahydrate,

0.5% formic acid, 1.2% sodium chloride, 0.17% of a dimethyl polysiloxane oil (softener), and the amounts of formaldehyde indicated below. After the treatment with the aqueous solution, the yarns were dried at 200°F. The treated yarns were then woven into the borders of cotton towels with the results indicated in the following Table:

TABLE I

Sample	Molar Ratio Formaldehyde: Methyl Carbamate	% Formaldehyde		% Nitrogen		
		Yarn in Finished Towel	Yarn in Towel Laundered 30 Times	Yarn In Finished Towel	Yarn In Towel Laundered 30 Times	Border* Pull-In In 30 Launderers
1	5.0:1	0.28	0.30	0.05	0.05	-0.2
2	7.5:1	0.56	0.56	0.07	0.07	-0.8
3	10.0:1	0.77	0.72	0.08	0.04	-1.9
4	12.5:1	1.13	0.95	0.07	0.07	-1.2
5	Untreated Control	—	—	0.03	0.07	6.3
(Treated Yarn Average)				0.058	0.052	

$$\text{*Border Pull-in} = \frac{\text{Width of Towel Body} - \text{Width of Towel Border}}{\text{Width of Towel Body}} \times 100$$

(i.e., Differential Shrinkage)

If the methyl carbamate had been affixed to the yarn, the amount of nitrogen would have been at least 0.26% for the sample having 1.13% of formaldehyde in the yarn (Sample 4).

The strength retention of the yarns treated

in this Example was very good. It is significant that strength retention was not dependent upon the level of formaldehyde fixed in the yarn. The strength retention is indicated in the following Table.

TABLE 2

Sample	Skein Breaking Strength	% Retention	Single End Break	% Retention
1	298	72	5.32	71
2	306	74	5.33	71
3	316	77	5.37	72
4	316	77	5.63	75
5—Control	411	—	7.48	—

The strength retentions appearing above were based on bleached, mercerized yarn taken immediately before treatment with methyl

carbamate and formaldehyde. When the strength retention calculation is based on the greige, mercerized yarn (6.37 lb. single end

break), the state at which yarn strength is normally determined, strength retention of the above yarns is from 80 to 88 per cent.

EXAMPLE II

- 5 Cotton yarn in a Kier was saturated with an aqueous mixture containing 0.5% magne-

sium chloride hexahydrate, 0.5% formic acid, 0.3% methyl carbamate and the indicated amounts of formaldehyde. The yarns were then vacuum extracted and dried at 180°F to 2—3% residual moisture.

TABLE II

Sample	% Formaldehyde in Mix	% Formaldehyde on Scoured Yarn	Molar Ratio Formaldehyde to Methyl Carbamate
1	1.5	0.37	12.5:1
2	1.5	0.40	12.5:1
3	2.5	0.52	20.8:1
4	2.7	0.52	22.5:1

- 15 The amount of fixed formaldehyde on the yarn is usually about 20 to 25% of the formaldehyde content of the aqueous mixture.

EXAMPLE III

An aqueous mixture containing 5% formaldehyde, 1% methyl carbamate and 1% mag-

nesium chloride hexahydrate was padded on a bleached enameling cotton duck at 55—60% wet pickup. The fabric was barely dried at 180°F (about 10% moisture), and heated at the indicated temperatures and times.

TABLE 4

Temperature °F.	Time Minutes	% Formaldehyde ⁽²⁾ Fixed on Fabric	% Nitrogen on Fabric	Appearance Rating ⁽¹⁾		Warp Shrinkage ⁽¹⁾	
				5L	20L	5L	20L
220	5	0.52	0.07	4.0	3.5	4.3%	4.1%
260	3	0.47	0.08	3.0	4.0	2.8	2.5
300	2	0.50	0.08	3.5	4.0	2.4	2.1
340	1	0.57	0.09	4.0	4.0	1.9	2.0
300	15	0.58	0.09	3.5	3.0	3.3	3.5
Control	—	—	0.04	—	—	8.3	—

⁽¹⁾ Determined on fabric laundered five and twenty times in an automatic washer with a rated capacity of 8 lbs. Fabric load was 8 lbs.; wash temperature was 105°F.; fabric was tumbled dried in an automatic clothes dryer. Rated on AATCC 5 (best) to 1 (poor) scale.

⁽²⁾ Fabric scoured one hour at 200°F. in 0.25% chip soap and 0.50% soda ash, followed by thorough rinsing.

25

EXAMPLE IV

In another set of samples using a mercerized and bleached 136×64 cotton broadcloth, an aqueous solution containing 2.5% form-

aldehyde, 1.0% methyl carbamate and catalyst as noted was applied at 60% wet pickup. The fabric was barely dried at 180°F. (about 10% moisture) and heated at 260°F. for 3 minutes.

30

TABLE 5

Sample	Catalyst System	% Formaldehyde ⁽¹⁾ Fixed	% Nitrogen		Crease Angles Dry	Recovery (W+F) Wet
			Before Scour	After Scour		
1	$\begin{cases} 1\% \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \\ 1\% \text{HCOOH} \end{cases}$	0.72	0.08	0.07	252°	212°
2	1% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	0.70	0.05	0.08	259°	246°
3	1% HCOOH	0.70	0.02	0.02	245°	234°
4	0.1% NH_4Cl ⁽²⁾	0.70	0.08	0.10	257°	242°
Control	—	—	0.02	0.04	127°	159°

(¹) Fabric scoured one hour at 200°F. in 0.25% chip soap and 0.50% soda ash followed by thorough rinsing.

(²) Estimated. Bath was neutral — NH_4Cl residual from preceding treatment of fabric.

Again only traces of nitrogen were found in the treated fabric, but it is important to note that the carbamate is not present on the fabric immediately after heating. This may be a clue in the determination of the mechanism of the reaction, because the carbamate is evidently decomposed by heating. A number of other samples have confirmed this observation.

EXAMPLE V

Bleached, mercerized cotton yarn was treated in a kier with an aqueous solution containing 2.5% formaldehyde, 1.36% sodium chloride, 0.5% magnesium chloride hexahydrate, 0.5% formic acid, 0.1% dimethyl polysiloxane oil and the indicated amounts of methyl carbamate, and later dried at 180°F.

TABLE 6

Sample	Mole Ratio Formaldehyde to Methyl Carbamate	% Methyl Carbamate	% Formaldehyde Fixed
1	62.5:1	0.1	0.30
2	20.8:1	0.3	0.52
3	8.9:1	0.7	0.76
4	6.25:1	1.0	0.20
5	12.5:1	0.5	0.33

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EXAMPLE VI

A bleached, mercerized cotton yarn in a kier was treated with an aqueous solution containing 1.3% sodium chloride, 0.5% magnesium chloride hexahydrate, 0.5% formic

acid, 0.1% dimethyl polysiloxane, 0.3% methyl carbamate and the indicated amounts of formaldehyde. The treated yarn was dried at 180°F.

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TABLE 7

Sample	Mole Ratio Formaldehyde to Carbamate	% Formaldehyde in Solution	% Formaldehyde Fixed
1	7.5:1	0.9	0.24
2	12.5:1	1.5	0.40
3	17.5:1	2.1	0.34
4	22.5:1	2.7	0.52

EXAMPLE VII

- 5 Mercerized cotton yarn was treated in a kier with an aqueous solution of 0.5% ethyl carbamate, 2.1% formaldehyde (mole ratio formaldehyde to carbamate of 12.5:1), 0.5% magnesium chloride and 0.5% formic acid. The yarn was dried at 200°F to fix the formaldehyde to the yarn.
- 10 The ability of the carbamate-formaldehyde process of the present invention to reduce swelling of fabrics is shown in the following Examples in the treatment of needle punched non-woven rayon fabrics.
- 15 Thus, a fabric which consists of an 8 oz. viscose rayon non-woven web (sold under the Trade Mark Avril) needled into a 1.6 oz. polypropylene scrim, calendered and palmered had an objectionable tendency to swell and increase in gauge during wet processing. This
- 20 objection can be overcome in part by using a combination of polypropylene fibre and viscose rayon for the web. Because of the thermoplasticity of the polypropylene, this combination of fibres in the web can be hot calendered and palmered to reduce the gauge of the base fabric and to reduce swelling and gauge increase during predipping. However,
- 25 this fabric still swelled and increased in gauge on wetting. Furthermore, the inclusion of the polypropylene fibres was a relatively expensive solution to the problem.

EXAMPLE VIII

- 35 The fabrics employed were as follows:
- (a) 8 oz. viscose rayon (Avril) web needle punched into a 1.6 oz. polypropylene scrim fabric,
- (b) 8 oz. 60% polypropylene 40% 8 oz. viscose rayon (Avril) web needle punched into
- 40 a 1.6 oz. polypropylene scrim fabric,
- (c) 3.3 oz. 60% polypropylene 40% viscose

rayon (Avril) web needled into a 1.0 oz. cotton scrim fabric.

Fabrics (a), (b) and (c) were all needled, calendered and palmered.

The aqueous mixture applied to the fabrics contained:

methyl carbamate	1%	
formaldehyde	4%	
magnesium chloride	0.83%	50
formic acid	0.83%	
nonylphenol-ethylene oxide adduct (wetting agent)	0.2%	

This mixture is called Formulation A hereinafter.

Formulation A was applied at 120°F. in a laboratory padder. Fabrics (a) and (b) were dried in a continuous oven at 250°F. and fabric (c) was dried in the oven at 220°F., the fabrics were rolled up and held in a convection oven at 220°F. for 1 1/2 hours to simulate conditions obtained if the fabric should be wound up hot in commercial production. Thermocouples embedded in the fabric rolls indicated the temperature on the inside of the fabric roll to be

When placed in the oven	125°F.	
After 25 minutes	170°F.	
After 45 minutes	185°F.	
After 1 hour and 30 minutes	200°F.	70

The gauges of these fabrics, before and after treatment, were measured with a Starrett Model 1010 spring loaded hand micrometer with a 1/4 inch anvil and 1/4 inch foot. The gauge was also measured after wetting in water.

	% Fixed Formaldehyde	Gauge (Dry)	Gauge (Saturated in Water)
Fabric (a) not treated	0	40 mils	68 mils
Fabric (a) treated	0.66%	45 "	59 "
Fabric (b) not treated	0	40 "	41 "
Fabric (b) treated	0.51%	34 "	36 "
Fabric (c) not treated	0	22 "	29 "
Fabric (c) treated	0.56%	23 "	25 "

5 The treated sample in each pair had an appreciably lower wet gauge than did the fabric not treated. The treatment also caused further compression and restriction of fabric (b), a fabric which as constructed was devised to restrict swelling. The formaldehyde fixation in this and the following Examples is based on the total weight of the fabric.

10 EXAMPLE IX

The fabrics employed were as follows:

(a) 8 oz. viscose rayon web needle punched into a 1.6 oz. polypropylene scrim fabric, calendered and palmered,

15 (b) 8 oz. 60% viscose rayon 40% polypropylene web needled into a 1.6 oz. polypropylene scrim,

20 (c) 8 oz. 60% viscose rayon 40% polypropylene web needled into a 1.6 oz. polypropylene scrim, calendered and palmered.

The treating solutions were:

Formulation A (See Example VIII)

Formulation B (the same as formulation A, except it contained 8% of formaldehyde)

25 Formulation C (the same as Formulation A except it contained 2% methyl carbamate and 8% formaldehyde).

30 The formulations were all applied at room temperature in a laboratory padder and vacuum extracted.

The fabrics were dried in a laboratory con-

tinuous dryer set at 260°F. The fabric treated with Formulation A attained a surface temperature of 232°F., the fabric treated with Formulation B attained a surface temperature of 214°F., and the fabric treated with Formulation C attained a surface temperature of 210°F. These differences in temperature had an influence on the level of formaldehyde fixed in the fabric.

40 After drying, these fabrics were treated with sodium bisulphite solution to remove formaldehyde odour and recatalyzed with an aqueous mixture containing 0.83% each of MgCl₂ and formic acid. The fabrics were then dried to the touch in a 300°F. oven after the washing and recatalyzation.

The fabrics were hot calendered on a two-roll calender at 250°F. and then palmered two passes at 260°F. on one drum of a two-drum compressive shrinkage machine.

50 The swelling effect was determined as in Example VIII by gauging the fabric dry, saturated with water and saturated with NaOH solution. Swelling characteristics were checked as finished in the laboratory (before calendering), after calendering and after calendering and palmering, the results of these tests and of formaldehyde analyses are set forth in the following table:

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Fabric	Formulation	% Fixed CH ₂ O	Gauge (Dry)	Gauge Saturated With Water	Gauge Saturated With 20% NaOH
(a)	Not treated	0	42 mils	54 mils	70 mils
(a)	A Before calendered	0.72	47	48	58
(a)	A Calendered	—	36	47	54
(a)	A Calendered and palmered	0.77	36	45	54
(a)	B Before Calendered	0.60	45	47	58
(a)	B Calendered	—	36	47	53
(a)	B Calendered and palmered	0.47	32	44	56
(a)	C Before Calendered	0.56	45	47	57
(a)	C Calendered	—	41	47	54
(a)	C Calendered and palmered	0.45	34	47	62
(b)	Not treated	0	62	58	68
(b)	A Before calendered	0.44	53	55	54
(b)	A Calendered	—	40	43	45
(b)	A Calendered and palmered	0.46	40	40	47
(c)	Not treated	0	28	32	42
(c)	A Before calendered	0.53	20	30	36
(c)	A Calendered	—	28	29	34
(c)	A Calendered and palmered	0.46	25	26	35

It is clear that the tendency of all of these fabrics in Example IX to swell in either water or in 20% NaOH has been reduced. Fabric (b) not treated, Gauge (Dry) is an artificially high value because this particular fabric was in the fluffy condition. If it were in the normal compressed condition of the other fabrics, it would have had a gauge considerably below 58.

For significant reduction in the swelling of the fabrics, the fabrics usually contain a substantial amount of cellulose fibres, e.g. 10% or more, usually at least 20%.

Examples X and XI demonstrate the speed at which processing of fabric is possible. They also demonstrate the rapidity of the reaction which occurs under very favourable conditions.

EXAMPLE X

Three lightweight white fabrics containing blends of 65% polyester fibre and 35% cotton fibre were processed through an aqueous mixture containing 1.0% methyl carbamate, 6.0% formaldehyde, 0.83% magnesium chloride, 0.83% formic acid, 0.5% acrylic polymer, comprising ethyl acrylate, methyl methacrylate, acrylic acid and acrylamide (Rhoplex E-32),